

APPENDIX F

Partition Coefficients For Lead

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F.1.0 Background

The review of lead K_d data reported in the literature for a number of soils led to the following important conclusions regarding the factors which influence lead adsorption on minerals, soils, and sediments. These principles were used to evaluate available quantitative data and generate a look-up table. These conclusions are:

- Lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.
- Anionic constituents such as phosphate, chloride, and carbonate are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation.
- A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH.
- Adsorption of lead increases with increasing organic matter content of soils.
- Increasing equilibrium solution concentrations correlates with decreasing lead adsorption (decrease in K_d).

Lead adsorption behavior on soils and soil constituents (clays, oxides, hydroxides, oxyhydroxides, and organic matter) has been studied extensively. However, calculations by Rickard and Nriagu (1978) show that the solution lead concentrations used in a number of adsorption studies may be high enough to induce precipitation. For instance, their calculations show that lead may precipitate in soils if soluble concentrations exceed about 4 mg/l at pH 4 and about 0.2 mg/l at pH 8. In the presence of phosphate and chloride, these solubility limits may be as low as 0.3 mg/l at pH 4 and 0.001 mg/l at pH 8. Therefore, in experiments in which concentrations of lead exceed these values, the calculated K_d values may reflect precipitation reactions rather than adsorption reactions.

Based on lead adsorption behavior of 12 soils from Italy, Soldatini *et al.* (1976) concluded that soil organic matter and clay content were 2 major factors which influence lead adsorption. In these experiments, the maximum adsorption appeared to exceed the cation exchange capacity

(CEC) of the soils. Such an anomaly may have resulted from precipitation reactions brought about by high initial lead concentrations used in these experiments (20 to 830 mg/l).

Lead adsorption characteristics of 7 alkaline soils from India were determined by Singh and Sekhon (1977). The authors concluded that soil clay, organic matter, and the calcium carbonate influenced lead adsorption by these soils. However, the initial lead concentrations used in these experiments ranged from 5 to 100 mg/l, indicating that in these alkaline soils the dominant lead removal mechanism was quite possibly precipitation.

In another adsorption study, Abd-Elfattah and Wada (1981) measured the lead adsorption behavior of 7 Japanese soils. They concluded that soil mineral components which influenced lead adsorption ranged in the order: iron oxides>halloysite>imogolite, allophane>humus, kaolinite>montmorillonite. These data may not be reliable because high lead concentrations (up to 2,900 mg/l) used in these experiments may have resulted in precipitation reactions dominating the experimental system.

Anionic constituents, such as phosphate, chloride, and carbonate, are known to influence lead reactions in soils either by precipitation of minerals of limited solubility or by reducing adsorption through complex formation (Rickard and Nriagu, 1978). A recent study by Bargar *et al.* (1998) showed that chloride solutions could induce precipitation of lead as solid $PbOHCl$. Presence of synthetic chelating ligands such as ethylenediaminetetraacetic acid (EDTA) has been shown to reduce lead adsorption on soils (Peters and Shem, 1992). These investigators showed that the presence of strongly chelating EDTA in concentrations as low as 0.01 M reduced K_d for lead by about 3 orders of magnitude. By comparison quantitative data is lacking on the effects of more common inorganic ligands (phosphate, chloride, and carbonate) on lead adsorption on soils.

A number of adsorption studies indicate that within the pH range of soils (4 to 11), lead adsorption increases with increasing pH (Bittel and Miller, 1974; Braids *et al.*, 1972; Griffin and Shimp, 1976; Haji-Djafari *et al.*, 1981; Hildebrand and Blum, 1974; Overstreet and Krishnamurthy, 1950; Scudato and Estes, 1975; Zimdahl and Hassett, 1977). Griffin and Shimp (1976) also noted that clay minerals adsorbing increasing amounts of lead with increasing pH may also be attributed to the formation of lead carbonate precipitates which was observed when the solution pH values exceeded 5 or 6.

Solid organic matter such as humic material in soils and sediments are known to adsorb lead (Rickard and Nriagu, 1978; Zimdahl and Hassett, 1977). Additionally, soluble organic matter such as fulvates and amino acids are known to chelate soluble lead and affect its adsorption on soils (Rickard and Nriagu, 1978). Gerritse *et al.* (1982) examined the lead adsorption properties of soils as a function of organic matter content of soils. Initial lead concentrations used in these experiments ranged from 0.001 to 0.1 mg/l. Based on adsorption data, the investigators expressed K_d value for a soil as a function of organic matter content (as wt.%) and the distribution coefficient of the organic matter. The data also indicated that irrespective of soil organic matter content, lead adsorption increased with increasing soil pH (from 4 to 8). In

certain soils, lead is also known to form methyl- lead complexes (Rickard and Nriagu, 1978). However, quantitative relationship between the redox status of soils and its effect on overall lead adsorption due to methylation of lead species is not known.

Tso (1970), and Sheppard *et al.* (1989) studied the retention of ^{210}Pb in soils and its uptake by plants. These investigators found that lead in trace concentrations was strongly retained on soils (high K_d values). Lead adsorption by a subsurface soil sample from Hanford, Washington was investigated by Rhoads *et al.* (1992). Adsorption data from these experiments showed that K_d values increased with decreasing lead concentrations in solution (from 0.2 mg/l to 0.0062 mg/l). At a fixed pH of 8.35, the authors found that K_d values were log-linearly correlated with equilibrium concentrations of lead in solution. Calculations showed that if lead concentrations exceeded about 0.207 mg/l, lead-hydroxycarbonate (hydrocerussite) would probably precipitate in this soil.

The K_d data described above are listed in Table F.1.

F.2.0 Approach

The initial step in developing a look-up table consisted of identifying the key parameters which were correlated with lead adsorption (K_d values) on soils and sediments. Data sets developed by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) containing both soil pH and equilibrium lead concentrations as independent variables were selected to develop regression relationships with K_d as the dependent variable. From these data it was found that a polynomial relationship existed between K_d values and soil pH measurements. This relationship (Figure F.1) with a correlation coefficient of 0.971 (r^2) could be expressed as:

$$K_d \text{ (ml/g)} = 1639 - 902.4(\text{pH}) + 150.4(\text{pH})^2 \quad (\text{F.1})$$

The relationship between equilibrium concentrations of lead and K_d values for a Hanford soil at a fixed pH was expressed by Rhoads *et al.* (1992) as:

$$K_d \text{ (ml/g)} = 9,550 C^{-0.335} \quad (\text{F.2})$$

where C is the equilibrium concentration of lead in $\mu\text{g/l}$. The look-up table (Table F.2) was developed from using the relationships F.1 and F.2. Four equilibrium concentration and 3 pH categories were used to estimate the maximum and minimum K_d values in each category. The relationship between the K_d values and the 2 independent variables (pH and the equilibrium concentration) is shown as a 3-dimensional surface (Figure F.2). This graph illustrates that the highest K_d values are encountered under conditions of high pH values and very low equilibrium lead concentrations and in contrast, the lowest K_d values are encountered under lower pH and higher lead concentrations. The K_d values listed in the look-up table encompasses the ranges of pH and lead concentrations normally encountered in surface and subsurface soils and sediments.

Table F.1. Summary of K_d values for lead adsorption on soils.

Soil Description	Clay Content (wt.%)	Organic Carbon (wt.%)	Iron Oxide content (wt.%)	pH	CEC (meq/100g)	K_d (ml/g)	Experimental Parameters	Reference
Sediment, Split Rock Formation, Wyoming	--	--	--	2.0	--	20	--	Haji-Djafari <i>et al.</i> , 1981
	--	--	--	4.5	--	100	--	
	--	--	--	5.75	--	1,500	--	
	--	--	--	7.0	--	4,000	--	
Sand (Soil C) Sand (Soil C) Sandy Loam (Soil D) Sandy Loam (Soil D)	0	--	--	4.5	22	280	Batch Experiment	Gerritse <i>et al.</i> (1982)
	0	--	--	5.0	22	1295	Batch Experiment	
	2	--	--	7.5	16	3,000	Batch Experiment	
	2	--	--	8.0	16	4,000	Batch Experiment	
Loam (Soil 2) Medium Sand (Soil 3) Organic soil (Soil 4) Fine Sandy Loam (Soil 6)	15	--	--	7.3	17	21,000	Batch Experiment	Sheppard <i>et al.</i> (1989)
	2	--	--	4.9	5.8	19	Batch Experiment	
	<1	--	--	5.5	120	30,000	Batch Experiment	
	11	--	--	7.4	8.7	59,000	Batch Experiment	
Sand (Hanford)	0.06	<0.01	0.41	8.35	5.27	13,000 - 79,000	Batch tracer studies	Rhoads <i>et al.</i> (1992)
							(Initial activities 2.38 - 23.4 $\mu\text{Ci/l}$)	

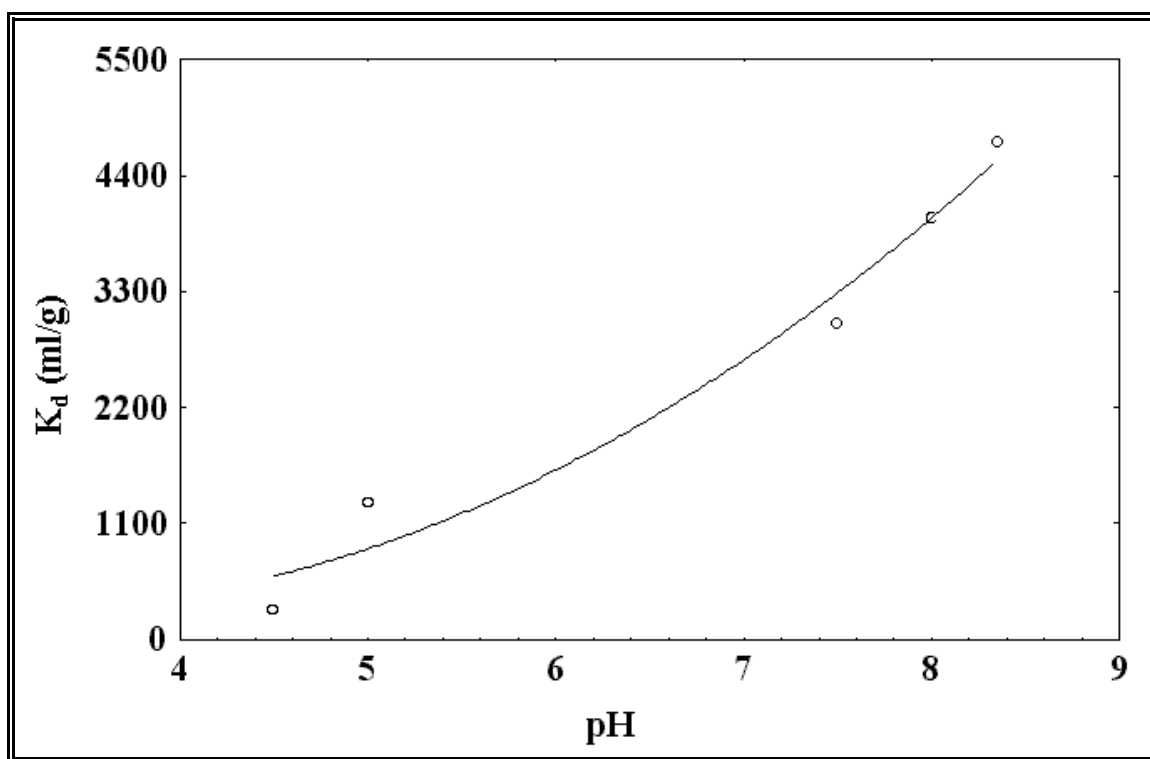


Figure F.1. Correlative relationship between K_d and pH.

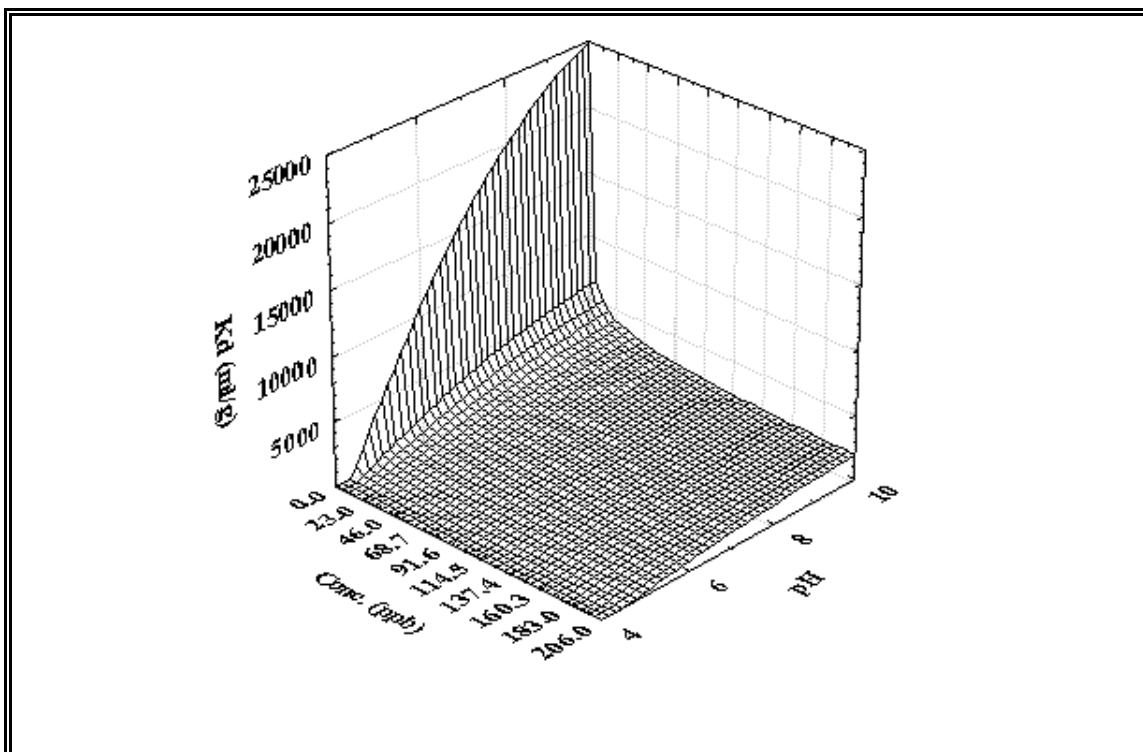


Figure F.2. Variation of K_d as a function of pH and the equilibrium lead concentrations.

F.3.0 Data Set for Soils

The data sets developed by Gerritse *et al.* (1982) and Rhoads *et al.* (1992) were used to develop the look-up table (Table F.2). Gerritse *et al.* (1982) developed adsorption data for 2 well-characterized soils using a range of lead concentrations (0.001 to 0.1 mg/l) which precluded the possibility of precipitation reactions. Similarly, adsorption data developed by Rhoads *et al.* (1992) encompassed a range of lead concentrations from 0.0001 to 0.2 mg/l at a fixed pH value. Both these data sets were used for estimating the range of K_d values for the range of pH and lead concentration values found in soils.

Table F.2. Estimated range of K_d values for lead as a function of soil pH, and equilibrium lead concentrations.

Equilibrium Lead Concentration ($\mu\text{g/l}$)	K_d (ml/g)	Soil pH		
		4.0 - 6.3	6.4 - 8.7	8.8 - 11.0
0.1 - 0.9	Minimum	940	4,360	11,520
	Maximum	8,650	23,270	44,580
1.0 - 9.9	Minimum	420	1,950	5,160
	Maximum	4,000	10,760	20,620
10 - 99.9	Minimum	190	900	2,380
	Maximum	1,850	4,970	9,530
100 - 200	Minimum	150	710	1,880
	Maximum	860	2,300	4,410

F.4.0 References

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